

STABILITY OF SCHWERTMANNITE AND COBALT SUBSTITUTED SCHWERTMANNITE IN MINING ENVIRONMENTS

SAMANTHA SCHONBERGER, Beloit College

Research Advisor: James Rougvie

INTRODUCTION

Acid mine drainage (AMD) is a problematic source of water pollution worldwide (Hudson-Edwards 2003; Antelo et al. 2013). Some trace metals (e.g., Cu, Co, Mn) found in AMD are useful micronutrients for organisms until they reach toxic concentrations (Romero et al. 2011). Fortunately, trace metals may be naturally removed from solution in mining environments through association with secondary minerals (e.g. jarosite, goethite, schwertmannite, etc.) formed due to weathering of mine waste. When trace metals adsorb onto the secondary minerals, the trace metals sit on the surface of the mineral due to a weak electrostatic bond (Regenspurg and Peiffer 2005). With coprecipitation, the trace metal is incorporated into the secondary mineral structure in a supposedly more stable form.

The secondary mineral schwertmannite [ideally $\text{Fe}_{16}\text{O}_{16}(\text{SO}_4)_2(\text{OH})_{12}$] was discovered by Udo Schwertmann in 1990 in an acidic stream in Austria (Schwertmann et al. 1995). A yellow-orange, semi crystalline, relatively unstable iron oxyhydroxide, schwertmannite has a high surface area that interacts with aqueous environments. Schwertmannite typically precipitates in Fe-rich, acidic environments over a pH range of 2.8-4.5 (Bigham et al. 1996). Other secondary minerals found with schwertmannite may include ferrihydrite, goethite, and jarosite depending on the pH levels and SO_4 concentrations (Dold 2003; Liao et al. 2009; Kawano and Tomita 2001).

Schwertmannite is a candidate mineral in the precipitates found in Blackbird Creek and Panther Creek in the Blackbird Mining district of Idaho,

which is described in this issue (Kimball 2016). In schwertmannite, Co^{2+} is expected to substitute for Fe^{3+} based on similar atomic radius, with charge balance maintained by periodic site vacancies. This study explored the behavior of Co substituted into synthesized schwertmannite under environmentally relevant leaching conditions. The main objectives were to: (1) compare leaching of synthesized schwertmannite (Swt) and cobalt-substituted schwertmannite (CoSwt) over a 20 day batch experiment; and (2) relate the experimental results to natural samples of stream water and precipitates taken from Blackbird Creek. Broadly, this research improves our understanding of how substituted trace metals affect the long-term stability of secondary minerals. More specifically this research helps us predict the mobility of cobalt in environments like Blackbird Creek.

METHODS

Schwertmannite was synthesized using a modified protocol from Cornell and Schwertmann (1996) published by Jones et al. (2006). Co-schwertmannite was prepared in the same manner, except Co^{2+} was present in the starting solution. Laboratory and field samples were characterized using standard analytical techniques including X-ray diffraction (XRD), scanning electron microscopy (SEM), and inductively coupled plasma mass spectrometry (ICP-MS). Analytical work was supplemented with calculations made using the thermodynamic modeling program PHREEQC. The experiments, analytical techniques, and thermodynamic calculations are described in more detail by Kimball (2016).

RESULTS

X-ray diffraction results showed peaks for schwertmannite on day 0, day 6, and day 20 for both Swt and CoSwt. The synthesized minerals matched PDF# 00-047-1775 in the RDB database before and after leaching. Images obtained by SEM also confirmed synthesis of Swt (Fig. 1) and CoSwt. Grains exhibited the typical radiating habit on day 0 (described by Dold 2003). The grains maintained a round shape but lost the spindles throughout leaching (similar to Acero et al. 2006).

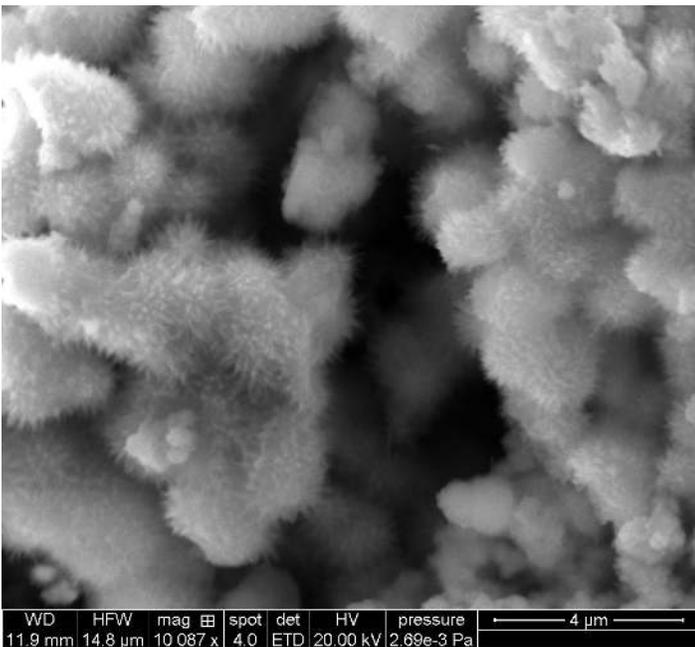


Figure 1. Swt-0 SEM image of a carbon-coated sample. Schwertmannite exhibits a radiating habit, creating high surface area for reaction with solution. The scale bar represents 4 µm.

In the Swt experiment, solution pH dropped by about 0.25 units relative to the Blank right away, then remained steady before dropping another 0.13 units between days 10 and 20 (Fig. 2). Likewise, in the CoSwt experiment, solution pH dropped by about 0.2 units relative to the Blank, remained relatively stable, then dropped another 0.2 units between days 10 and 20 (Fig. 2). The pH in the Swt leach was slightly lower than that in the CoSwt leach for the duration of the experiment. Slight variations in pH overtime followed a similar pattern for the Blank, Swt, and CoSwt (Fig. 2).

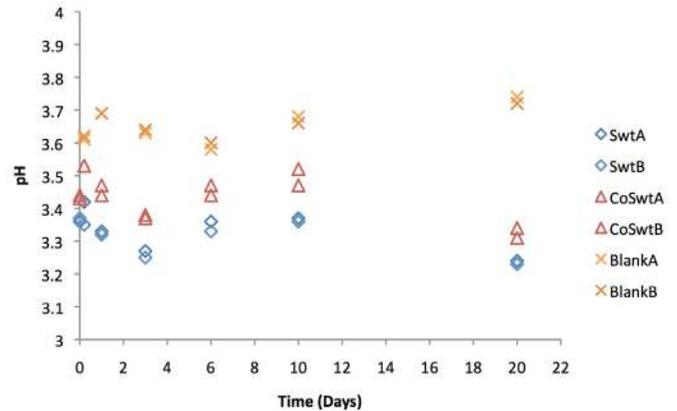


Figure 2. Solution pH over time during batch leach experiments. Both Swt and CoSwt leachates show lower pH than the Blank, with the Swt experiment being most acidic.

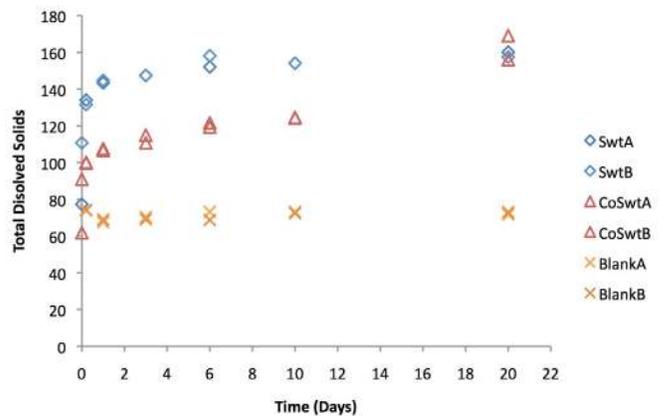


Figure 3. Total Dissolved Solids over time during batch leach experiments. Generally, both Swt and CoSwt values increase rapidly the first day, then plateau, with Swt values higher than CoSwt values. CoSwt TDS values for day 20 were calculated with PHREEQC because of a failing conductivity meter.

The total dissolved solids (TDS) remained stable in the Blank experiment, but increased rapidly during the first day before reaching a plateau in the Swt experiment (Fig. 3). The CoSwt solution showed similar changes in TDS (although to a lesser extent compared to Swt) until after day 10, after which TDS decreased. Calibration for conductivity on the instrument became more difficult for day 20, so the TDS data are likely incorrect due to instrumental error. Using PHREEQC to calculate TDS on day 20 gives 156 mg/L (CoSwtA) and 169 mg/L (CoSwtB), which is more consistent with related results (Fig. 3).

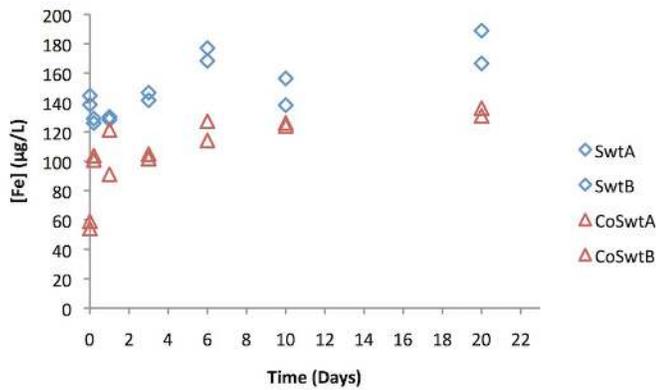


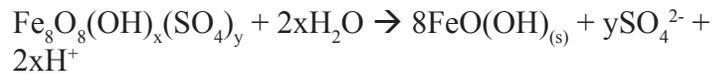
Figure 4. Dissolved Fe concentrations over time during batch leach experiments. Dissolved Fe concentrations generally increase steadily until day 6, then remain stable in both experiments.

In the Swt experiment, dissolved Fe increased steadily from about 140 to 180 µg/L, whereas in the CoSwt experiment dissolved Fe increased steadily from about 60 to 130 µg/L (Fig. 4). In the CoSwt experiment, dissolved Co concentrations increased rapidly during the first day, then remained stable around 30 µg/L for the remainder of the experiment. Dissolved SO₄ concentrations (data not shown) calculated by charge balance in PHREEQC generally mirrored pH changes because H⁺ was the predominant cation in solution during the experiment.

DISCUSSION

The results show that the majority of change in Swt and CoSwt leach solutions happened during the first few days (Fig. 3, Fig. 4). Both Swt and CoSwt showed a lower pH than the Blank, with Swt having a lower pH than CoSwt. This suggests that Swt exhibited a higher amount of dissolution than CoSwt, increasing the amount of H⁺ ions in solution, and thereby increasing the acidity.

To understand the stability of the minerals, it is useful to reference a possible dissolution reaction. The general formula for schwertmannite in this experiment is assumed to be: [Fe₈O₈(OH)_x(SO₄)_y], where x=8-2y, and 1 < y < 1.75 (Bigham et al. 1990). Since pH dropped by day 20, we expect a dissolution reaction for schwertmannite that has H⁺ as a product. The following proposed reaction from Paikaray and Peiffer (2010) supports the pH data:



Schwertmannite is known to be metastable, and it is possible for it to transform into goethite [FeO(OH)] over a timescale of weeks to months (Acero et al. 2006). The XRD results were referenced to see if any peaks could have represented goethite, but only schwertmannite peaks were detected. Even though no evidence was found for goethite, it is possible that it was present below detection, or over a longer period of time a transformation could have occurred.

The total dissolved solids (TDS) data show that Swt values were higher than CoSwt values, which supports Swt having been dissolved more than CoSwt, except by day 20, when TDS values were similar for both experiments (Fig. 3). Increased TDS at the end of the CoSwt experiment is consistent with decreased pH, and increased Fe, Co, and SO₄ concentrations. The amount of dissolved Fe was higher for Swt than CoSwt, which is consistent with lower pH and higher TDS in Swt solutions compared to CoSwt solutions and further supports that Swt dissolved more than CoSwt. These results may signal that Swt was less stable than CoSwt over the 20-day leach period (Fig. 4).

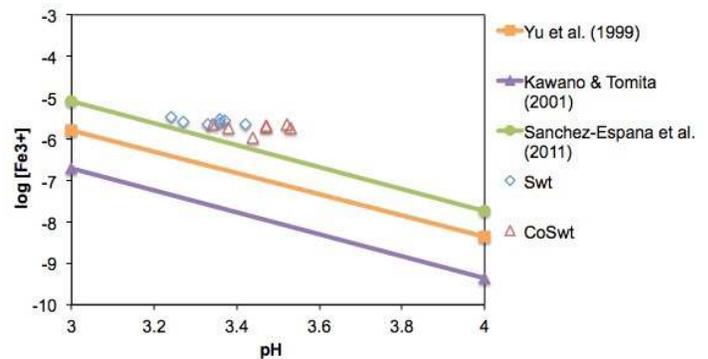


Figure 5. Plot of log[Fe³⁺] against pH with experimentally determined schwertmannite solubility lines. Schwertmannite solubility lines are as follows: log[Fe³⁺]=0.125logK - alogSO₄ - bpH, where a and b were equal to 0.2176 and 2.563 (Yu et al. 1999), 0.1313 and 2.738 (Kawano and Tomita 2001), and 0.175 and 2.65 (Sánchez-España et al. 2011). Swt and CoSwt data points evolved to become closer to equilibrium over the 20-day leach period.

Thermodynamic data for schwertmannite vary over 10 orders of magnitude (Fig. 5). Figure 5 shows dissolved Fe concentrations and pH values for Swt and CoSwt leach experiments as well as experimentally determined solubility lines, which separate the schwertmannite stability field (above the line) and the solution stability field (below the line). Since the data points fall above the solubility lines, the mineral is predicted to be the most stable phase at the given conditions and assuming the system has established equilibrium. The experiment did not begin under equilibrium conditions, however, and the data points for both Swt and CoSwt plot farther from the lines and get closer to equilibrium over the 20-day period. When the system was farthest from equilibrium, we saw the most rapid change shown by the dramatic change in slope for day 1 in the figures for pH (Fig. 2), TDS (Fig. 3), and Fe concentrations (Fig. 4). The intent of the experiment was to observe how Swt and CoSwt changed over time under conditions where schwertmannite is expected to be stable, so the experiment was conducted in the low pH environment where schwertmannite is often observed. Figure 5 shows that over time, the solution evolved towards equilibrium, with Swt solutions poised to establish equilibrium before CoSwt solutions. In both experiments, dissolved Fe concentrations begin to stabilize around day 6, which is consistent with the system establishing equilibrium with a solid Fe phase (Fig. 4).

When comparing leach results in this study to those for goethite (Penprase 2016) and jarosite (Anthony 2016), Swt and CoSwt solutions exhibited the lowest pH and the highest TDS of all the minerals tested. All of the results combined support the expectation that schwertmannite is the least stable of the minerals (Murad and Rojik 2005). This is also consistent with schwertmannite transforming into one of the more stable minerals jarosite and/or goethite (Acero et al. 2006, Kawano and Tomita 2001, Antelo et al 2013). In terms of Co release to solution, CoSwt maintained a dissolved Co concentration near 30 $\mu\text{g/L}$ during most of the experiment. During leaching of Co-substituted goethite, dissolved Co concentrations were around 700 $\mu\text{g/L}$ for the first 6 days, then remained near 250 $\mu\text{g/L}$ for the rest of the experiment (Penprase 2016). Similar experiments with Co-substituted jarosite showed a

nearly linear release of Co over time, increasing at 4.5 $\mu\text{g/L}$ per day and reaching about 90 $\mu\text{g/L}$ by day 20 (Anthony 2016). These results suggest that even though schwertmannite itself is less stable, it is better able to sequester substituted Co relative to goethite and jarosite.

Experimental results did not easily relate to the field samples since Swt was not detected in the precipitates collected from Blackbird Creek. The lack of Swt could be because the samples collected were the freshest precipitates, which were likely amorphous based on XRD analysis (Penprase 2016). However, since many mining sites contain schwertmannite, the experimental results can be applied to other locations.

CONCLUSION

Results from this study show that during leaching under conditions where schwertmannite was expected to be stable, CoSwt appeared to be more stable than Swt. The implication of these results is that trace metal substituted schwertmannite may be more stable than relatively pure schwertmannite. This result is encouraging given that schwertmannite in the environment is most likely to contain trace elements. While CoSwt was more stable than Swt, however, Co still dissolved out of the mineral. Because this is the first study to experiment with Co-substituted schwertmannite, further research is needed to better predict the long-term behavior of Co substituted into schwertmannite to understand the role it plays in areas affected by Co mining activities.

ACKNOWLEDGEMENTS

I would like to acknowledge the Keck Geology Consortium for making this research possible. I would like to thank Dr. Bryn Kimball for her guidance, immense knowledge on the research topic, and tireless interest in helping me improve. I would like to thank Dr. James Rougvie for his ever-present support and advice. I am grateful for the support received from fellow Keck students, Jason Anthony and Shanti Penprase, and Whitman student Lena Goss. Laboratory experiments and SEM and XRD analysis were conducted at Whitman College. Further SEM and XRD were conducted at Carleton College.

REFERENCES

- Aceró, P., Ayora, C., Torrentó, C., and Nieto, J.-M., 2006, The behavior of trace elements during schwertmannite precipitation and subsequent transformation into goethite and jarosite: *Geochimica et Cosmochimica Acta*, v. 70, p. 4130–4139.
- Antelo, J., Fiol, S., Gondar, D., Perez, C., Lopez, R., and Arce, F., 2013, Cu(II) incorporation to schwertmannite: Effect on stability and reactivity under AMD conditions: *Geochimica et Cosmochimica Acta*, v. 119, p. 149–163.
- Bigham, J., Schwertmann, U., Carlson, L., and Murad, E., 1990, A poorly crystallized oxyhydroxysulfate of iron formed by bacterial oxidation of Fe(II) in acid-mine waters: *Geochimica et Cosmochimica Acta*, v. 54, p. 2743–2758.
- Bigham, J.M., Schwertmann, U., Traina, S.J., Winland, R.L., and Wolf, M., 1996, Schwertmannite and the chemical modeling of iron in acid sulfate waters: *Geochimica et Cosmochimica Acta*, v. 60, p. 2111–2121.
- Cornell, R.M., and Schwertmann, U., 1996, *The Iron Oxides: Structure, Properties, Reactions, Occurrence and Uses*: Hoboken, NJ, John Wiley & Sons, 491 p.
- Dold, B., 2003, Dissolution kinetics of schwertmannite and ferrihydrite in oxidized mine samples and their detection by differential X-ray diffraction (DXRD): *Applied Geochemistry*, v. 18, p. 1531–1540.
- Hudson-Edwards, K.A., 2003, Sources, mineralogy, chemistry and fate of heavy metal-bearing particles in mining-affected river systems: *Mineralogical Magazine*, v. 67, p. 205–217.
- Jones, E.J.P., Nadeau, T.-L., Voytek, M.A., and Landa, E.R., 2006, Role of microbial iron reduction in the dissolution of iron hydroxysulfate minerals: *Journal of Geophysical Research-Biogeosciences*, v. 111, p. G01012.
- Kawano, M., and Tomita, K., 2001, Geochemical modeling of bacterially induced mineralization of schwertmannite and jarosite in sulfuric acid spring water: *American Mineralogist*, v. 86, p. 1156–1165.
- Liao, Y., Zhou, L., Liang, J., and Xiong, H., 2009, Biosynthesis of schwertmannite by *Acidithiobacillus ferrooxidans* cell suspensions under different pH condition: *Materials Science & Engineering C-Biomimetic and Supramolecular Systems*, v. 29, p. 211–215.
- Murad, E., and Rojik, P., 2005, Iron mineralogy of mine-drainage precipitates as environmental indicators: review of current concepts and a case study from the Sokolov Basin, Czech Republic: *Clay Minerals*, v. 40, p. 427–440.
- Paikaray, S., and Peiffer, S., 2010, Dissolution kinetics of sulfate from schwertmannite under variable pH conditions: *Mine Water and the Environment*, v. 29, p. 263–269.
- Regenspurg, S., and Peiffer, S., 2005, Arsenate and chromate incorporation in schwertmannite: *Applied Geochemistry*, v. 20, p. 1226–1239.
- Romero, A., González, I., and Galán, E., 2011, Stream water geochemistry from mine wastes in Peña de Hierro, Riotinto area, SW Spain: a case of extreme acid mine drainage: *Environmental Earth Sciences*, v. 62, p. 645–656.
- Sánchez-España, J., Yusta, I., and Diez-Ercilla, M., 2011, Schwertmannite and hydrobasaluminite: A re-evaluation of their solubility and control on the iron and aluminium concentration in acidic pit lakes: *Applied Geochemistry*, v. 26, p. 1752–1774.
- Yu, J.Y., Heo, B., Choi, I.K., Cho, J.P., and Chang, H.W., 1999, Apparent solubilities of schwertmannite and ferrihydrite in natural stream waters polluted by mine drainage: *Geochimica et Cosmochimica Acta*, v. 63, p. 3407–3416.